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ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR MATERIALS  
(U) MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE  
AND ENGINEERING F E KARASZ SEP 83 AFOSR-TR-84-0903

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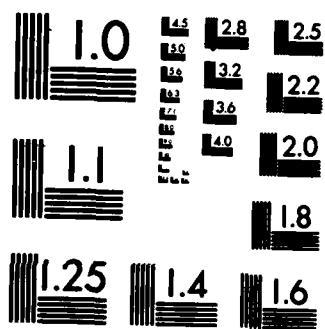
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AFOSR-TR- 84 - 0903

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FINAL REPORT

ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR MATERIALS

AFOSR

Contract F49620-83-K-0006

1 October 1982 - 30 September 1983

Frank E. Karasz  
Polymer Science and Engineering  
University of Massachusetts  
Amherst, Massachusetts 01003

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**REPORT DOCUMENTATION PAGE**

1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			4. PERFORMING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) <b>AFOSR-TR- 34-0903</b>		
6a. NAME OF PERFORMING ORGANIZATION Polymer Science & Engineering Univ of Massachusetts		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC		
6c. ADDRESS (City, State and ZIP Code) Amherst, MA 01003		7b. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR		8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-83-K-0006		
8c. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling AFB, DC 20332		10. SOURCE OF FUNDING NOS.			
		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303	TASK NO. A3	WORK UNIT NO.
11. TITLE (Include Security Classification) Ultrastructure Processing of Macromolecular Materials					
12. PERSONAL AUTHOR(S) Frank E. Karasz					
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 1 Oct 82 TO 30 Sep 83	14. DATE OF REPORT (Yr., Mo., Day) Sep 83		15. PAGE COUNT 14	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	Electroactive polymers      Epoxy plasticization		
			Ultrastructural domains      Rigid Rod Polymers		
			Polymer blends      Block Copolymers		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  See reverse					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input checked="" type="checkbox"/> DTIC USERS <input type="checkbox"/>			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL DR. DONALD R. ULRICH		22b. TELEPHONE NUMBER (Include Area Code) (202) 767-4963		22c. OFFICE SYMBOL NC	

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This research has as one of its principal aims the development of electroactive polymers with ultrastructural domains. This research program also incorporates investigations in polymer blends, epoxy plasticization, characterization of rigid rod polymers and other areas. The ultrastructure portion consists of a coordinated research effort with Profs. R. Lenz and H. Winter into the synthesis of electrically conducting block copolymers, the structuring of such materials by novel techniques, and the characterization of the polymers produced. Recent advances in this area are described as follows. In the studies of polymer blends various lines of research have been pursued that have recently proved most revealing. These include problems of compatibility in polymer-copolymer systems, the effects of crystallization, and of pressure. The studies of plasticization with water and other diluents in network and in semi-crystalline polymers has continued to use new techniques such as deuterium quadrupole NMR and neutron scattering. Various theoretical studies in the area of fluids were also extended. Quasi-elastic light scattering was used further to characterize assymetric solutes and suspensoids. High pressure studies of polymer liquid crystals were initiated to elucidate the thermodynamics of such systems. The cooperative ultrastructure research has capitalized on recent synthetic and processing advances. In this effort Prof. Lenz has extended his synthetic efforts in the area of polyphenylene vinylene and related block copolymers while polyvinyl pyridine was studied further. Prof. Winter investigated structures produced in shear and extensional flow fields.

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Polymer Science and Engineering  
University of Massachusetts  
Amherst, Massachusetts 01003

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#### ACKNOWLEDGEMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald L. Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to Dr. Donald R. Ulrich, Program Manager, Directorate of Chemical Sciences, and to other members of the Directorate, for their unfailing cooperation, help and courtesy extended to him during the period of this contract.

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I. TITLE: Ultrastructure Processing of Molecular Materials

II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz  
Polymer Science and Engineering  
University of Massachusetts  
Amherst, Massachusetts 01003

III. CONTRACT NUMBER: F49620-83-K-0006

IV. DATES: 1 October 1982 - 30 September 1983

V. SENIOR RESEARCH PERSONNEL: S. Akiyama  
T. Ellis  
X. Jin  
Y. Maeda  
B. H. Su  
G. ten Brinke  
H. Ueda

VI. JUNIOR RESEARCH PERSONNEL: M. Bishop  
J. Capistran  
L. Falces  
A. Finkenaur  
S. Friedrich  
S. Kuehl  
C. Lee  
F. Morrison  
H. S. Park  
C. Perry  
D. Rougie  
J. Schroeder  
G. Tovstiga

## VII. ABSTRACT OF ACCOMPLISHMENTS

This report describes research at the MIRP at the University of Massachusetts which has as one of its principal aims the development of electroactive polymers with ultrastructural domains. This research program also incorporates investigations in polymer blends, epoxy plasticization, characterization of rigid rod polymers and other areas. The ultrastructure portion consists of a coordinated research effort with Profs. R. Lenz and H. Winter into the synthesis of electrically conducting block copolymers, the structuring of such materials by novel techniques, and the characterization of the polymers produced. Recent advances in this area are described below.

In the studies of polymer blends we have pursued various lines of research that have recently proved most revealing. These include problems of compatibility in polymer-copolymer systems, the effects of crystallization, and of pressure. The studies of plasticization with water and other diluents in network and in semi-crystalline polymers has continued to use new techniques such as deuterium quadrupole NMR and neutron scattering. Various theoretical studies in the area of fluids were also extended. Quasi-elastic light scattering was used further to characterize asymmetric solutes and suspensions. High pressure studies of polymer liquid crystals were initiated to elucidate the thermodynamics of such systems. The cooperative ultrastructure research has capitalized on recent synthetic and processing advances. In this effort Prof. Lenz has extended his synthetic efforts in the area of polyphenylene vinylene and related block copolymers while polyvinyl pyridine was studied further. Prof. Winter investigated structures produced in shear and extensional flow fields.

## VIII. DESCRIPTION OF RESEARCH ACCOMPLISHED

The research performed during the contract period is divided into several categories as indicated below. A large fraction of the results have been published or are in press. Thus, whenever possible the descriptive matter in this section has been condensed by referring to the appropriate publication(s) which are listed in Section IX.

### A. Polymer Blends

Several major advances were achieved during the past year. In particular we wish to cite the theoretical progress in the area of compatibilization of homopolymer-copolymer systems. For some years we have been studying systems containing poly(2,6-dimethyl phenylene oxide) and partially (or totally) halogenated polystyrene. Some seemingly peculiar features were observed: for example it was found that PPO and poly-o-chlorostyrene, and PPO and poly-p-chlorostyrene were incompatible, whereas random copolymers of the two isomers were readily miscible with PPO. This observation has now been rationalized and, moreover, the resulting theory can be used to predict similar effects in other systems and to calculate interaction parameters. We have also completed a study of the effect of tacticity on polymer blends using the model syndiotactic and isotactic polymethyl methacrylate system. The effect of pressure on this blend is novel in several respects. Crystallization of isotactic polystyrene in PPO-PS blends has also been investigated in detail and we have thereby discovered techniques of separating thermodynamic and kinetic effects, (1\*,2,8,13,14,15,21,25,26).

\*These numbers correspond to publications listed in section IX.

B. Network Polymers

Our original hypothesis regarding the effect of water on epoxies (i.e. that the massive  $T_g$  depression observed could be explained on a thermodynamic basis without invoking special interactions) has now been extensively verified in a number of network polymer-diluent systems. In the last year we have investigated epoxy-water compositions more thoroughly with systematic variations in network density and chemical structure. We have also extended the concept to physically crosslinked systems (i.e. semi-crystalline polymers) with very good agreement. By using deuterium oxide (heavy water) as a diluent we have made the system amenable to investigation by quadrupole NMR techniques and this has yielded valuable new insights, (7,12,16,24).

C. Ultrastructured Conducting Polymers

The goal of this investigation has been to prepare block or graft copolymers which will form two distinct phases in the solid state, and in which one of the phases will be electrically conducting and the other not. To achieve this objective, the block or graft copolymers must be initially, at least, fusible or soluble so that well controlled and well characterized two-phase systems can be formed, and the phase structure must be maintained after doping one of the polymers to form the conducting phase.

One of the polymers for the conducting phase, which was selected for our initial study, was poly-2-vinylpyridine, PVP, which can be doped with either iodine or TCNB. This polymer can be obtained as a "living polymer" by anionic initiators, so AB block copolymers were prepared with both polystyrene, PS, and

polybutadiene, PB, as the A blocks, which form the insulating phase and PVP as the B block for the conducting phase, as follows:

Sample	A Block	PVP B Block Weight %	Calculated Molecular Weight		$\bar{M}_w/\bar{M}_w$ Observed
			Total	PVP B Block	
I	PB	40	70,000	28,000	1.1
II	PB	60	52,000	31,000	1.2
III	PS	36	65,000	26,000	1.2

The three diblock copolymers prepared, as described above, could be solution cast into films that contained well developed two phase systems, which could be clearly seen by electron microscopy after selectively obtaining either the phase with osmium tetroxide, OsO<sub>4</sub>, or the PVP phase with iodine or methyl iodide. In Polymer I PVP forms the continuous phase because the film was cast from a good solvent for this polymer. On annealing above the T<sub>g</sub> of PVP, phase inversion occurs and the PB phase becomes the matrix while the PVP phase becomes the spherical domains. Hence, considerable control can be achieved over the phase morphology by the manner in which the film is obtained as well as by variation of polymer composition.

A second polymer under investigation, which has the potential of developing on doping conductivities as high as those of doped polyacetylenes, is polyphenylene vinylene, PPV. In all previous investigations described in the literature, this polymer has not been prepared in sufficiently high enough molecular weights from doped films for conductivity studies. However, we have

investigated a new polymerization reaction by which we have been able to obtain strong films of the polymer by solution casting and reacting a precursor polymer. These films could be doped with iodine to form a metallic-like appearance; the conversion of the precursor film to the PPV film has been quantitatively achieved, and relatively high conductivities were obtained.

D. Extensional Flow Processing

A new technique has been developed for subjecting small polymeric samples to well defined extensional strains. The sample is introduced between two metal plates which are coated with a lubricant fluid. The sample is squeezed (thickness  $H(t)$ ) when the metal plates are driven together at a prescribed rate. the lubricant reduces the shear stresses in the sample to a level which is negligibly small. The resulting strain is called equibiaxial or planar extension, depending whether the shape of the plates is circular or rectangular. The instrument allows for measuring the squeezing force as well as the squeezing rate. Transient equibiaxial extensional viscosities as measured in this new device have been obtained. It should be mentioned here that this is the first time that such an extensional viscosity has ever been measured for a molten polymer. The technique has been proposed and tested in a simple bench experiment by Chataei, Macosko, and Winter (1982) for PDMS gums at room temperature. during the last year, the technique was developed further and is now capable of stretching at high temperatures and at prescribed rates.

E. Other Investigations

In the contract period some twenty seven publications were published as a result of AFOSR support (see next section). Several other research areas have proved fruitful and we shall summarize these below.

1. Composites with covalently bonded interfaces, (5,6,18).
2. Conformational transitions in ordered systems, (10,19,20).
3. Theoretical studies of fluids, (4,9,17,22).
4. Characterization of polymers, (3,11,23,27).

## IX. PUBLICATIONS

1. *Thermochimica Acta*, 54, 349-356 (1982) (with R. Vukovic, V. Kuresevic, and W. J. MacKnight)  
"The Investigation of the Compatibility and Phase Separation of Poly (2,6-Dimethyl-1,4-Phenylene Oxide) and Styrene-fluorosubstituted Styrene Copolymer Blends by Differential Scanning Calorimetry".
2. *Polymer Compatibility* (K. Solc. Ed.) MMI Press, Midland, Michigan (1982), p. 165-175 (with W. J. MacKnight)  
"Solid State Properties of Polymer Blends"
3. *Macromolecules* 15, 1083-1088 (1982) (with J. M. O'Reilly, and H. E. Bair)  
"Thermodynamic Properties of Stereoregular Poly(methyl methacrylate)".
4. *J. Chem. Phys.* 77 (10), 5249-5250 (1982) (with G. ten Brinke)  
"Scaling Theory and Enthalpy of Mixing for Binary Fluids".
5. *Polymer Engineering and Science* 22, 968-974 (1982) (with V. P. Chacko and R. J. Farris)  
"Dynamic Mechanical Behavior of Filled Polyethylenes and Model Composites".
6. *J. Poly. Sci.* 20, 2177-2195 (1982) (with V. P. Chacko, R. J. Farris, E. L. Thomas)  
"Morphology of CaCO<sub>3</sub>-Filled Polyethylenes".
7. *J. Appl. Poly. Sci.* 28, 23-32 (1983) (with T. S. Ellis, G. ten Brinke)  
"The Influence of Thermal Properties on the Glass Transition Temperature in Styrene/Divinylbenzene Network-Diluent Systems".
8. *J. Appl. Poly. Sci.* 28, 219-224 (1983) (with R. Vukovic, W. J. MacKnight)  
"Compatibility of Some Fluorosubstituted Styrene Polymers and Copolymers in Blends with Poly(2,6-Dimethyl-1,4-Phenylene Oxide) and with Polystyrene".
9. *J. Chem. Phys.*, 78, 995-996 (1983) (with G. ten Brinke)  
"An Improved Upper Bound for the Free Energy of a Single Chain Lattice Model".
10. *Int. J. Biol. Macromol.* 5, 53-56 (1983) (with G. E. Gajnos and D. C. Lu)  
"Conformational Stability of Deuterated Poly(Beta-Benzyl-L-Aspartate) in m-Cresol".
11. *J. Matl. Sci.* 18, 721-729 (1983) (with R. K. Galkiewicz)  
"Viscoelastic Characterization of Poly(Butylene Terephthalate) using Longitudinal Resonances".
12. *Macromolecules* 16, 244-249 (1983) (with G. ten Brinke and T. S. Ellis)  
"Depression of Glass Transition Temperature of Polymer Networks by Diluents".



13. J. Appl. Poly. Sci., 28, 1379-1389 (1983) (with R. Vukovic, V. Kuresevic, N. Segudovic, and W. J. MacKnight)  
"Compatibility of Poly(2,6-Dimethyl-1,4-Phenylene Oxide)/Poly(Fluorostyrene-Co-Chlorostyrene) Blends".
14. Macromolecules 16, 381-387 (1983) (with S. L. Zacharius, G. ten Brinke, and W. J. MacKnight)  
"Evidence for Critical Double Points in Blends of Polystyrene and Poly(o-chlorostyrene)".
15. Polymer 24, 529-533 (1983) (with R. Vukovic and W. J. MacKnight)  
"Compatibility of Poly(p-fluorostyrene-co-ofluorostyrene) with poly(2,6-dimethyl-1,4-phenylene oxide) and polystyrene".
16. Macromolecules 16, 1019 (1983) (with L. W. Jelinski, J. J. Dumais, R. E. Stark, and T. S. Ellis)  
"The Interaction of Epoxy Resins with Water. A quadrupole Echo Deuterium NMR Study".
17. J. Chem. Phys. 79, 2065-2071 (1983) (with Gerrit ten Brinke)  
"The One-Dimensional no-o Vector Model and the Helix-Coil Transition".
18. J. Appl. Poly. Sci. 28, 2701-2713 (1983) (with V. P. Chacko and R. J. Farris)  
"Tensile Properties of CaCO<sub>3</sub>-Filled Polyethylenes".
19. Eur. Polym. J. 19, 1037-1041 (1983) (with K. Jeremic)  
"Heat Capacity Changes at the Helix-Coil Transition of Polypeptides in Mixed Organic Solvents".
20. Biopolymers 22, 2411-2421 (1983) (with P. R. Couchman, G. E. Gajnos, and C. L. Ryan)  
"Heat Capacity Increments: Conformational Transitions in Polypeptides".
21. Macromolecules 16, 1827-1832 (1983) (with G. ten Brinke and W. J. MacKnight)  
"Phase Behavior in Copolymer Blends: Poly(2,6-dimethyl-1,4phenylene oxide) and Halogen-Substituted Styrene Copolymers".
22. J. Chem. Phys. 78, 4792 (1983) (with G. ten Brinke)  
"Reply to the Comments by Morrison".
23. Analytical Calorimetry (J. Johnson and P. Gill, Eds.) Plenum Publishing Corp., N. Y., N. Y., (1984), p.325-341 (with E. Donoghue and T. Ellis)  
"The Effect of Sample Temperature Gradients on DSC Thermograms at the Glass Transition Temperature".

24. Polymer 25, 664 (1984) (with T. Ellis)  
"Interaction of Epoxy Resins with Water: the Depression of Glass Transition Temperature".
25. Polymer Blends and Composites in Multiphase Systems (C. D. Han, Ed.)  
American Chemical Society, Washington, D. C., (1984), p.17-32 (with  
S. L. Zacharius and W. J. MacKnight)  
"A Polymer Blend Exhibiting Both Upper and Lower Critical Solution  
Temperature Behavior: Polystyrene/Poly(o-chlorostyrene)".
26. Macromolecules 17, 810-814 (1984) (with J. Plans and W. J. MacKnight)  
"Equilibrium Melting Point Depression for Blends of Isotactic Polystyrene  
with Poly(2,6-dimethylphenylene oxide)".
27. J. Chem. Phys. 80(10) (1984) (with P. Russo and K. Langley)  
"Dynamic Light Scattering Study of Semidilute Solutions of a Stiff-Chain  
Polymer".

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